I. HYDROGEN BONDING AS A FACTOR IN SOLUBILITY
II. ATTEMPTS TO FORM CHELATE RINGS INVOLVING C-H←N AND C-H←O BONDS

BY

JAMES HARKEMA

A.B., Calvin College, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1941

Urbana, Illinois
1941

I. HYDROGEN BONDING AS A FACTOR IN SOLUBILITY
II. ATTEMPTS TO FORM CHELATE RINGS INVOLVING C-H←N AND C-H←O BONDS

BY
JAMES HARKEMA
A.B., Calvin College, 1937

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1941

Urbana, Illinois
1941

ACKNOWLEDGMENT

The writer wishes to express his sincere appreciation to Professor C. S. Marvel who initiated and so kindly directed this research.

I. HYDROGEN BONDING AS A FACTOR IN SOLUBILITY

Introduction

Since Latimer and Roedbush[1] first introduced the concept of hydrogen bonding it has found general application in explaining many abnormal effects of liquids and solids. One of the most important properties affected by hydrogen bonding is that of solubility. Abnormal solubilities are observed where an interaction of solvent and solute occurs due to hydrogen bonding. Hydrogen bonding is found when suitable "donor" and "acceptor" groups are present. The term "donor" atom or molecule is used to designate atoms or molecules containing an electron pair capable of being donated to form a hydrogen bond, such as in oxygen and nitrogen. "Acceptor" molecules are those containing a hydrogen atom capable of accepting a pair of electrons to form a hydrogen bridge or bond.

From the time of Sidgwick[2] who first related hydrogen bonding to solubility many abnormalities have been explained by the formation of O-H←O, O-H←N, N-H←N, and F-H←F bonds. In recent years[3-6] the relationship between solubility and hydrogen bonding has been extended to compounds containing the C-H group. Whenever the carbon is sufficiently substituted with negative groups the ionic character of the hydrogen is increased to such an extent that it is capable of coordination with the donor groups, such as those in esters, ketones, ethers and disubstituted amides. Hydrogen bonding explains the abnormal solubilities in donor solvents of halogenated compounds of the type CHX_3, CH_2X_2, HCX_2CX_3 and similar compounds where X is chlorine or fluorine. Heats of mixing[7-9] and infra-red absorption spectra[10-13] have verified the presence of hydrogen bonding in these cases and have extended the acceptor groups to the acetylenic hydrogen in phenylacetylene and the S-H hydrogen in thiophenol.

The present work arises from the need for more infor-

mation concerning the solubility of solid donor molecules in weak hydrogen bonding solutes containing C-H, S-H, O-H and N-H groups.

Experimental and Discussion

Solubilities of polyvinyl acetate, poly methyl vinyl ketone, poly methyl methacrylate, cellulose triacetate, polyvinyl chloride, and a sample of "vinylite" containing forty per cent polyvinylacetate and sixty per cent polyvinyl chloride were determined in phenylacetylene, thiophenol, 1-heptyne, dimethylethynylcarbinol, nitromethane, pyrrole, and N-methyl acetamide. High solubilities were observed for polyvinyl acetate, poly methyl vinyl ketone, poly methyl methacrylate, and "vinylite" which contain donor groups and low solubility for polyvinyl chloride, containing no donor group, in all the solvents except 1-heptyne and N-methyl acetamide. Although cellulose triacetate contains donor groups it is not highly soluble in most solvents, probably due to its high molecular weight. It dissolves to the greatest extent in pyrrole indicating the strong tendency to form N-H←O bonds. The low solubilities in 1-heptyne indicates weak acceptor properties. The activity of the hydrogen in N-methylacetamide is absorbed in its intermolecular association resulting in low solubilities. These results furnish additional evidence for hydrogen bonding due to the acceptor groups C-H, S-H, O-H, and N-H.

Bibliography

1. Latimer and Rodebush, J. Am. Chem Soc. **42**, 1419 (1920).
2. Sidgwick, "The Electronic Theory of Valency," Oxford Univ. Press, 1929.
3. Zellhoefer, Ind. Eng. Chem. **29**, 548 (1937).
4. Zellhoefer, Copley, and Marvel, J. Am. Chem Soc. **60**, 1337 (1938).
5. Copley, Zellhoefer, and Marvel, Ibid. **60**, 2666 (1938); Ibid. **60**, 2714 (1938); Ibid. **61**, 3580 (1939); Ibid. **62**, 227 (1940).
6. Marvel, Dietz and Copley, Ibid. **62**, 2273 (1940).
7. Zellhoefer and Copley. Ibid. **60**, 1343 (1938).
8. Copley and Holley, Ibid. **61**, 1599 (1939).
9. Marvel, Copley and Ginsberg, Ibid. **62**, 3109 (1940); Ibid **62**, 3263 (1940).
10. Buswell, Deitz and Rodebush, J. Chem. Phys. **5**, 84, 301 (1937).
11. Buswell, Rodebush and Roy, J. Am. Chem. Soc. **60**, 2444 (1938).
12. Gordy, J. Am. Chem. Soc. **60**, 605 (1938).
13. Gordy, J. Chem. Phys. **7**, 163 (1939).

II. ATTEMPTS TO FORM CHELATE RINGS INVOLVING C-H←N AND C-H←O BONDS

Introduction

Hydrogen bonding due to the C-H acceptor group has been established recently by solubility,[1] heats of mixing,[2] and infra-red absorption spectra.[3] Previously all the evidence for C-H bonding has concerned the bonds between different molecules or intermolecularly. The next logical step was to discover whether intramolecular bonding, "chelation", is possible. By suitable arrangement of donor and acceptor groups intramolecular hydrogen bridges should be formed.

Experimental and Discussion

A compound which should most likely form a chelate ring of the C-H←N type is the dimethylamide of ω-dichloro-o-toluic acid. It contains the strong donor group, a disubstituted amide, and a hydrogen attached to a carbon atom which is highly substituted with negative groups which increases the activity of the acceptor hydrogen. These groups are also suitably placed to form a six-membered ring. However, previous work in this laboratory indicated that this compound was very unstable and unsuitable for this study. It was then suggested that the hydrogen of the aliphatic carbon of triphenylmethane derivatives should be sufficiently active to act as an acceptor. The N, N-dimethylamide and the methyl ester of *o*-benzhydrylbenzoic acid were prepared and their properties compared with the corresponding para compounds which in contrast to the ortho compounds should show intermolecular bonding.

Molecular weight determinations and infra-red absorption spectra failed to show any chelate ring formation in the ortho esters due to a C-H←O bond or in the amides due to a C-H←N bond, or intermolecular association in the para compounds. The C-H←N bond would be expected to be formed in preference to the C-H←O also possible in the amides since previous evidence indicates that it is the stronger bond.

The molecular weights were measured in dry, thiophene-free benzene and all the compounds showed a normal increase in the apparent molecular weight values as the concentration was increased. The infra-red absorption spectra were taken in carbon-tetrachloride by Professor W. H. Rodebush who reported no indication of hydrogen bonding.

The *o*-benzhydrylbenzoic acid was prepared according to the method of Baeyer.[4] The methyl ester was prepared by esterification in three per cent solution of hydrogen chloride in methyl alcohol.

The method of Jones and Root[5] to prepare *o*-benzhydrylbenzoyl chloride proved to be unsatisfactory. Instead of heating the acid with thionyl chloride in carbon disulfide-chloroform mixture the acid was caused to react with a slight excess of thionyl chloride in ether solution at room temperature. The tendency to form the condensation product, 9-phenyl-9-chloroanthrone is minimized and a good yield of the acid chloride is obtained. The dimethylamide was then prepared easily by passing dry dimethylamine into an ether solution of the acid chloride.

The *p*-benzhydrylbenzoic acid was prepared according to the method of Bistrzycki and Cyr.[6] The ester was prepared by esterification in three per cent solution of hydrogen chloride in methyl alcohol. The dimethylamide was prepared by passing dry dimethylamine into an ether solution of the acid chloride.

Bibliography

1. References 3-6 of Part I.
2. References 7-9 of Part I.
3. References 10-13 of Part I.
4. Baeyer, Ann. **202**, 50 (1880).
5. Jones and Root, J. Am. Chem Soc. **48**, 190 (1926).
6. Bistrzycki and Cyr, Ber. **37**, 663 (1904).

VITA

The writer was born in Grand Rapids, Michigan on November 3, 1915. He attended the parochial Christian schools of that city and was graduated from Grand Rapids Christian High School in June, 1933. He entered Calvin College, Grand Rapids, Michigan, in the fall of 1933 and received the A. B. degree in June, 1937. In the fall of 1937 he entered the Graduate School of the University of Illinois, and served as an assistant in Analytical Chemistry for the years 1937-1941.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549818_0012